STN- Structure Search
4/19/06

10/536,613

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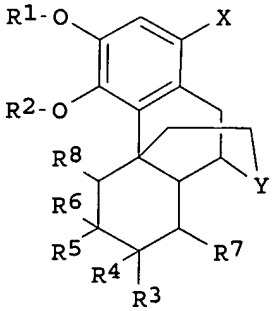
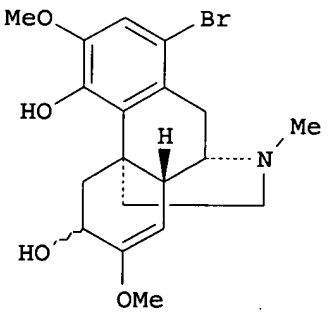
L4 ANSWER 1 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:467867 CAPLUS
DOCUMENT NUMBER: 141:23767
TITLE: Preparation of sinomenine compounds for the treatment of cognitive disorders
INVENTOR(S): Qin, Guo-Wei; Tang, Xi-Can; Wang, Rui; Zhou, Tian-Xi; Lestage, Pierre; Caignard, Daniel-Henri; Renard, Pierre
PATENT ASSIGNEE(S): Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Peop. Rep. China; Les Laboratoires Servier
SOURCE: PCT Int. Appl., 35 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2004048340	A1	20040610	WO 2003-EP14841	20031126
WO 2004048340	C1	20050707		
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW				
RW: BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
CN 1504469	A	20040616	CN 2002-153819	20021128
CA 2507067	AA	20040610	CA 2003-2507067	20031126
AU 2003290119	A1	20040618	AU 2003-290119	20031126
EP 1565444	A1	20050824	EP 2003-782481	20031126
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR, BG, CZ, EE, HU, SK				
BR 2003016609	A	20051011	BR 2003-16609	20031126
JP 2006509755	T2	20060323	JP 2004-554526	20031126
US 2006009480	A1	20060112	US 2005-536613	20050525
NO 2005003139	A	20050627	NO 2005-3139	20050627
PRIORITY APPLN. INFO.:			CN 2002-153819 A	20021128
			WO 2003-EP14841 W	20031126

OTHER SOURCE(S): MARPAT 141:23767
GI



I



II

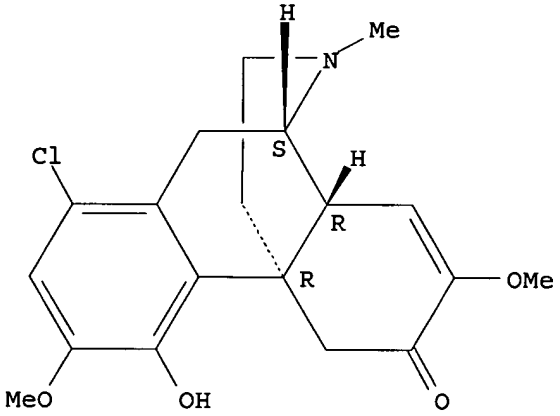
AB Sinomenine and compds. thereof of formula I [Y = (substituted) N, (substituted) N-oxide, disubstituted N+ halide; X = halo; R1 = alkyl; R2 = H, acyl; R3 = OH, alkoxy; R4, R7 = H; R4R7 = bond; R3R4 = oxo, (substituted) N; R5, R8 = H, R5R8 = bond; R6 = OH, acyl, etc.] are prepared The compds. are useful in the treatment of cognitive disorders. Pharmaceutical compns. containing I are described. Thus, II was prepared from sinomenine, and showed a difference of -36 s at a dose of 20 mg/kg in social recognition in the Wistar rat.

IT **700361-94-0P 700362-01-2P 700362-03-4P**
RL: PAC (Pharmacological activity); RCT (Reactant); SPN (Synthetic preparation); THU (Therapeutic use); BIOL (Biological study); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)
(preparation of sinomenine compds. for the treatment of cognitive disorders)

RN 700361-94-0 CAPLUS

CN Morphinan-6-one, 1-chloro-7,8-didehydro-4-hydroxy-3,7-dimethoxy-17-methyl-, (9α,13α)- (9CI) (CA INDEX NAME)

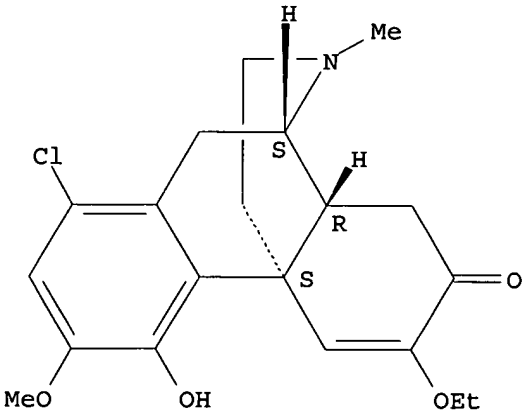
Absolute stereochemistry.



RN 700362-01-2 CAPLUS

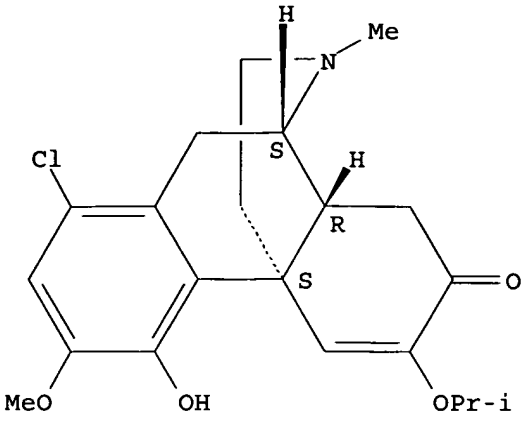
CN Morphinan-7-one, 1-chloro-5,6-didehydro-6-ethoxy-4-hydroxy-3-methoxy-17-methyl-, (9α,13α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



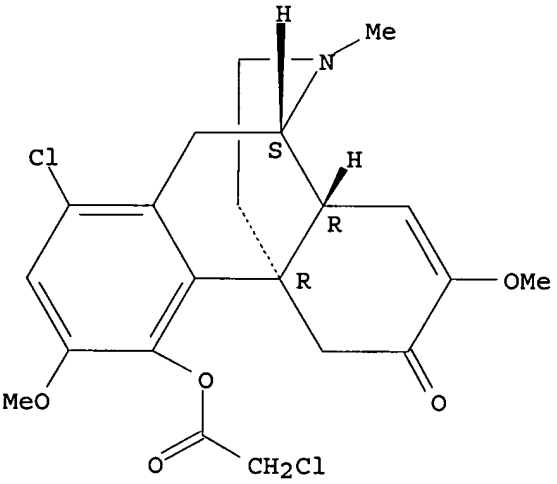
RN 700362-03-4 CAPLUS

CN Morphinan-6-one, 1-bromo-7,8-didehydro-4-hydroxy-3,7-dimethoxy-17-methyl-, (9α,13α,14β)- (9CI) (CA INDEX NAME)



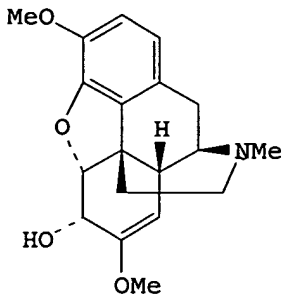
RN 700362-15-8 CAPLUS
CN Morphinan-6-one, 1-chloro-4-[(chloroacetyl)oxy]-7,8-didehydro-3,7-dimethoxy-17-methyl-, (9α,13α)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



REFERENCE COUNT: 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1978:609063 CAPLUS
DOCUMENT NUMBER: 89:209063
TITLE: Synthesis and antinociceptive activity of 7-methoxycodeine
AUTHOR(S): Iijima, Ikuo; Minamikawa, Junichi; Rice, Kenner C.; Jacobson, Arthur E.
CORPORATE SOURCE: Lab. Chem., Natl. Inst. Arthritis, Metab. Dig. Dis., Bethesda, MD, USA
SOURCE: Journal of Medicinal Chemistry (1978), 21(12), 1320-2
CODEN: JMCMAR; ISSN: 0022-2623
DOCUMENT TYPE: Journal
LANGUAGE: English
GI



I

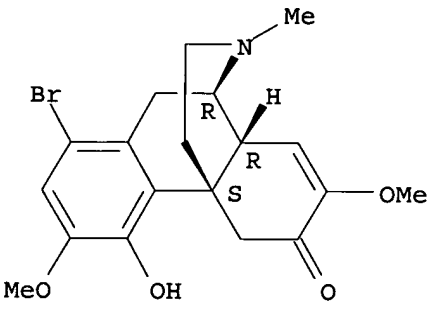
AB The title compound (I) [68160-82-7] was synthesized from (-)-1-bromosinomeninone [68170-84-3] by enol methylation, closure of the oxide bridge by treatment with Br2, and LiAlH4 reduction, and I was tested for antinociceptive activity. The introduction of the 7-MeO group into the C ring of codeine did not decrease its oral activity, but I was unstable in acidic media. Apparently, the oral activity of I was not due to its conversion to the acid-stable (-)-sinomeninone [2230-60-6], since the latter was orally inactive.

IT **68160-79-2P 68160-80-5P**
RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); THU (Therapeutic use); BIOL (Biological study); PREP (Preparation); USES (Uses)
(preparation and analgesic activity of)

RN 68160-79-2 CAPLUS

CN Morphinan-6-one, 1-bromo-7,8-didehydro-4-hydroxy-3,7-dimethoxy-17-methyl- (9CI) (CA INDEX NAME)

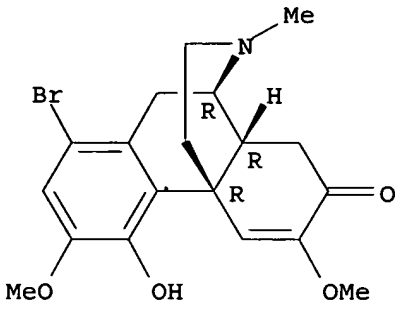
Absolute stereochemistry.



RN 68160-80-5 CAPLUS

CN Morphinan-7-one, 1-bromo-5,6-didehydro-4-hydroxy-3,6-dimethoxy-17-methyl- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

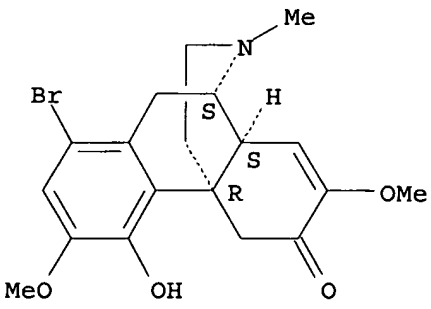


L4 ANSWER 3 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1934:6501 CAPLUS
DOCUMENT NUMBER: 28:6501
ORIGINAL REFERENCE NO.: 28:832b-d
TITLE: Physiological action of (-) and (+) derivatives of morphine alkaloids
AUTHOR(S): Goto, Kakuji
SOURCE: Proceedings of the Imperial Academy (Tokyo) (1933), 9, 390-3
CODEN: PIATA8; ISSN: 0369-9846
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

AB The physiol. actions of 6 pairs of morphine derivs. prepared from sinomenine (I) were studied. The (-) and (+) forms of dihydrocodeinone (II), dihydrotheobainone (III), β-tetrahydrodesoxycodeine (V), dihydrothebainol (V), 1-bromosinomenine (VI), and α-dihydrosinomenine (VII) were tested for toxicity, tail reaction, analgesic action, convulsant action, and influence on respiration and blood pressure. The d-derivs. of I are chiefly convulsive poisons and show no tail response, analgesic action or respiratory depression. In the l-derivs. II, III and IV display all these properties, but V has no convulsant action, VI shows only weak analgesic effects and VII provokes no tail reaction although the other characteristic reactions are pos. Conclusion: These properties of morphine derivs. depend on configuration as well as constitution.

IT **847941-31-5**, Sinomenine, 1-bromo-, l- (physiol. action of)
RN 847941-31-5 CAPLUS
CN Sinomenine, bromo- (3CI) (CA INDEX NAME)

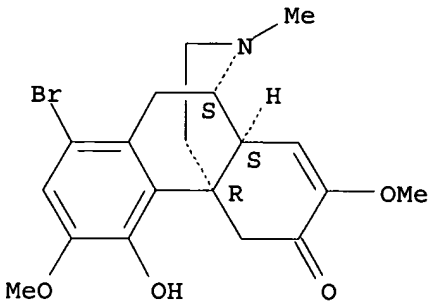
Absolute stereochemistry.



L4 ANSWER 4 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1931:8717 CAPLUS

DOCUMENT NUMBER: 25:8717
ORIGINAL REFERENCE NO.: 25:959b-g
TITLE: Partial syntheses in the morphine series. I
AUTHOR(S): Schopf, Clemens; Pfeifer, Theo
SOURCE: Ann. (1930), 483, 157-69
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB Dihydrothebainone (I) (35 g.) in 300 cc. AcOH treated with 16 g. Br in 150 cc. AcOH at 15° and the residue in 200 cc. H2O treated with 35 g. KI, gives 43.5 g. of the HI salt, m. 215° (decomposition), of 1-bromodihydrothebainone (II), m. 167°, crystals with 0.5 mol. AcOEt; HBr salt, m. 210-5° (decomposition); oxime, m.178-80°. II also results by the reduction of 1-bromodihydrocodeinone (III), m. 205-7°, with Zn and NH4Cl in EtOH. III is formed in 75-80% yield by treating I with 2 mols. Br and treating the residue with 7 N KOH; from II.HBr in MeOH with Br and then treating the residue with KOH (80% yield); and by bromination of dihydrocodeinone (IV) in AcOH. Reduction of III in AcOH-AcONa with Pd and H gives quant. IV. While the formation of the phenol group from the O bridge has been accomplished before, this is the first time the reverse reaction has been carried out. In the same way there was prepared 1-bromodihydrohydroxythebainone, m. 190-1°; with Br and alkali this gives 75-80% of 1-bromodihydrohydrocodeinone, m. 181-4°; catalytic reduction gives dihydrohydroxycodeinone. 1-Bromosinomenine, m. 188-9° (Goto and Nambo, C. A. 24, 4042), with Br and alkali, give 75% of 1-bromosinomeneine, m. 213° (this is the isobromosinomenine of G. and N.).
IT **847941-31-5**, Sinomenine, 1-bromo-
(preparation of)
RN 847941-31-5 CAPLUS
CN Sinomenine, bromo- (3CI) (CA INDEX NAME)

Absolute stereochemistry.



L4 ANSWER 5 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1930:37406 CAPLUS
DOCUMENT NUMBER: 24:37406
ORIGINAL REFERENCE NO.: 24:4042b-e
TITLE: Sinomenine and disinomenine. XVI. Isobromosinomenine (or bromosinomeneine)
AUTHOR(S): Goto, Kakuji; Nambo, Taro
SOURCE: Bulletin of the Chemical Society of Japan (1930), 5, 165-9
CODEN: BCSJA8; ISSN: 0009-2673
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB cf. C. A. 24, 3512. Isobromosinomenine (I) is always produced when sinomenine-HCl (II) is brominated in HOAc or C3H5CO2H. I is probablyan oxidized product and the above name would be inappropriate. G. and N. wish

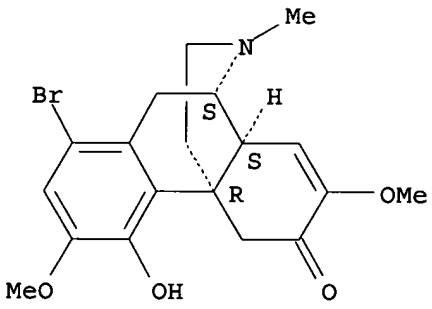
instead to call I bromosinomeneine and to substitute bromosinomeneine ketone (III) for isobromosinomeninone. II in HOAc with 1 mol. of Br gave 80% of bromosinomenine (IV), m. 153%, [α]D8 -8.87° (CHCl3); (HCl salt (+ 3H2O), m. 116°; HBr salt, m. 232° (from MeOH); oxime, softens 168°, decomps. 211°; methiodide, m. 80°), together with 2-20% of I. With 2 mols. of Br the above reaction gave 40% of I, m. 217° (from alc.), [α]D9 -83.03° (CHCl); HCl salt, m. 231° (decomposition); HBr salt, m. 229°; oxime, m. 162°; oxime HCl salt, softens 236°, m. 280°; methiodide, m. 211-2°. I heated in 2 N HCl at 100° gave III, m. 198° (from CHCl3), [α)D9, 119.89°; dioxime, m. 173.5° (decomposition); dioxime HCl salt, softens 208°, m. 195° (decomposition). When the bromination mixture containing IV was allowed to stand several weeks, IV was converted into sinomeninone, m. 227°; oxime, m. 189°; methiodide, m. 246°. From such reactions were isolated varying amts. of sinomenine hydrate, m. 157° (from alc.); [α]D7 41.85; oxime, m. 231°; methiodide, m. 192-5° (decomposition) (the previously published value, 264°, was an error).

IT **847941-31-5**, Sinomenine, bromo- (and derivs.)

RN 847941-31-5 CAPLUS

CN Sinomenine, bromo- (3CI) (CA INDEX NAME)

Absolute stereochemistry.



L4 ANSWER 6 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1930:32896 CAPLUS

DOCUMENT NUMBER: 24:32896

ORIGINAL REFERENCE NO.: 24:3512g-i,3513a

TITLE: Sinomenine and disinomenine. XV. Reduction of bromosinomenine with nascent hydrogen

AUTHOR(S): Goto, Kakuji; Inaba, Reikichi

SOURCE: Nippon Kagaku Kaishi (1921-47) (1930), 2, 53-8
CODEN: NIKWAB; ISSN: 0369-4208

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

AB cf. C. A. 24, 1385. The reduction of bromosinomenine (I) was studied by various methods and the results were compared with the previously published results on the reduction of sinomenine. The 2 compds. reacted in the same way with different reducing agents. I was reduced in 2% NaOH with Na-Hg. After 72 hrs. the H2O solution was saturated with CO2, the precipitate dissolved in CHCl3, evaporated and acetone added, precipitating 34.3% of granular 1,1'-dibromo-bis-8,8'-desmethoxydihydrosinomenine (II), m. 227°, darkens 274° (from acetone), [α]D13 19.02° (alc.); oxime, m. 237° (decomposition); methiodide, m. 253-5°. II was also prepared by the bromination of bis-8,8'-desmethoxydihydrosinomenine.

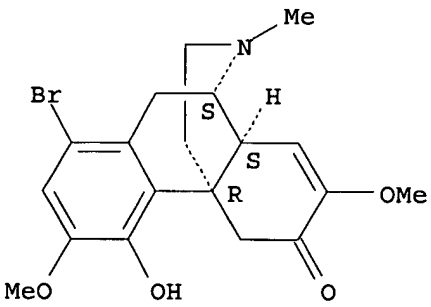
Bromodihydrosinomenine similarly reduced gave 35% of 1-bromodesmethoxysinomenine (III), m. 119° (from acetone), [α]D13 57.57° (alc.); oxime, m. 263°; methiodide, m. 127° (decomposition), sinters 119°. III was also prepared by the bromination of desmethoxydihydrosinomenine. I.HBr was reduced with Zn-Hg and HCl on the steam bath, with periodic addition of HCl (fuming), yielding 30% of bromodesmethoxydesoxodihydrosinomenine (IV), m. 127° (from acetone), [α]D12 40.44° (alc.); methiodide, m. 253-5°. IV was also prepared by the bromination of desmethoxydesoxodihydrosinomenine. β-Tetrahydrodesoxycodeine, m. 149°, was brominated in HOAc, yielding 50% of the Br derivative (C18H24BrNO2), m. 127° [α]D13 -39.52° (alc.). This and IV were mixed in alc. and evaporated, yielding a solid, m. 122° (decomposition), sinters 119°, optically active in alc. I reduced with ZnHCl gave bromodihydrosinomenine, m. 236°.

IT **847941-31-5**, Sinomenine, bromo-
(reduction of)

RN 847941-31-5 CAPLUS

CN Sinomenine, bromo- (3CI) (CA INDEX NAME)

Absolute stereochemistry.



L4 ANSWER 7 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1930:32895 CAPLUS

DOCUMENT NUMBER: 24:32895

ORIGINAL REFERENCE NO.: 24:3512g-i,3513a

TITLE: Sinomenine and disinomenine. XV. Reduction of bromosinomenine with nascent hydrogen

AUTHOR(S): Goto, Kakuji; Inaba, Reikichi

SOURCE: Bulletin of the Chemical Society of Japan (1930), 5, 93-8
CODEN: BCSJA8; ISSN: 0009-2673

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

AB cf. C. A. 24, 1385. The reduction of bromosinomenine (I) was studied by various methods and the results were compared with the previously published results on the reduction of sinomenine. The 2 compds. reacted in the same way with different reducing agents. I was reduced in 2% NaOH with Na-Hg. After 72 hrs. the H2O solution was saturated with CO2, the precipitate dissolved in CHCl3, evaporated and acetone added, precipitating 34.3% of granular 1,1'-dibromo-bis-8,8'-desmethoxydihydrosinomenine (II), m. 227°, darkens 274° (from acetone), [α]D13 19.02° (alc.); oxime, m. 237° (decomposition); methiodide, m. 253-5°. II was also prepared by the bromination of bis-8,8'-desmethoxydihydrosinomenine. Bromodihydrosinomenine similarly reduced gave 35% of 1-bromodesmethoxysinomenine (III), m. 119° (from acetone), [α]D13 57.57° (alc.); oxime, m. 263°; methiodide, m.

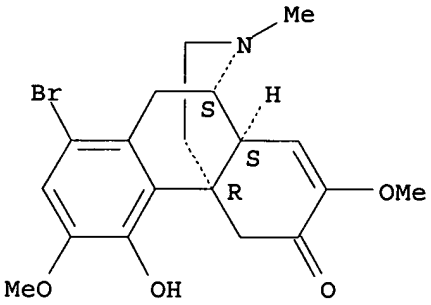
127° (decomposition), sinters 119°. III was also prepared by the bromination of desmethoxydihydrosinomenine. I.HBr was reduced with Zn-Hg and HCl on the steam bath, with periodic addition of HCl (fuming), yielding 30% of bromodesmethoxydesoxodihydrosinomenine (IV), m. 127° (from acetone), [α]D12 40.44° (alc.); methiodide, m. 253-5°. IV was also prepared by the bromination of desmethoxydesoxodihydrosinomenine. β-Tetrahydrodesoxycodeine, m. 149°, was brominated in HOAc, yielding 50% of the Br derivative (C18H24BrNO2), m. 127° [α]D13 -39.52° (alc.). This and IV were mixed in alc. and evaporated, yielding a solid, m. 122° (decomposition), sinters 119°, optically active in alc. I reduced with ZnHCl gave bromodihydrosinomenine, m. 236°.

IT **847941-31-5**, Sinomenine, bromo-
(reduction of)

RN 847941-31-5 CAPLUS

CN Sinomenine, bromo- (3CI) (CA INDEX NAME)

Absolute stereochemistry.



L4 ANSWER 8 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1930:5312 CAPLUS

DOCUMENT NUMBER: 24:5312

ORIGINAL REFERENCE NO.: 24:620i,621a

TITLE: Sinomenine and disinomenine. XIII. The reduction of bromosinomenine

AUTHOR(S): Goto, Kakuji; Nakamura, Teruko

SOURCE: Bulletin of the Chemical Society of Japan (1929), 4, 195-8
CODEN: BCSJA8; ISSN: 0009-2673

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

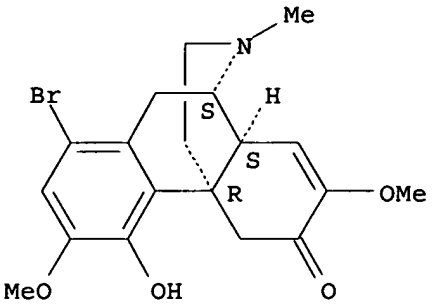
AB The bromination of sinomenine in AcOH leads to the formation of 2 isomeric bromosinomenines. Expts. on the oxidation, reduction and diazo reactions with these 2 compds. leads to the opinion that the Br atom in both the products is in the (1) position opposite the free OH group in the phenanthrene nucleus and it is assumed that the 3rd benzene ring of the phenanthrene nucleus has undergone some change in the case of isobromosinomenine.

IT **847941-31-5**, Sinomenine, bromo-
(reduction of)

RN 847941-31-5 CAPLUS

CN Sinomenine, bromo- (3CI) (CA INDEX NAME)

Absolute stereochemistry.



L4 ANSWER 9 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1929:31293 CAPLUS
DOCUMENT NUMBER: 23:31293
ORIGINAL REFERENCE NO.: 23:3709d-i,3710a-e
TITLE: Constitution of sinomenine
AUTHOR(S): Kondo, Heizaburo; Ochiai, Eiji
SOURCE: Ann. (1929), 470, 224-54
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB cf. J. Pharm. Society Japan Number 497, 503, 538; C. A. 22, 964-5, 4531. Sinomenine (I) is the principal alkaloid of the root of Sinomenium acutum, Rehd. et Wils., found in South Japan. I, liberated from the HCl salt with Na2CO3 and crystallized from C6H6, m. 161°, then solidifies and again m. 182°; the higher melting form is also obtained by adding NH4OH to the aqueous solution of the HCl salt; on standing it reverts to the lower melting form; analysis and mol. weight indicate the formula C19H23NO4; [α]26D -70.76° (0.2120 g. in 10 cc. EtOH); HCl salt, decomps. 231°, [α]17D -6.89° (4.1812 g. in 100 cc. H2O), crystals with 2 H2O; chloroaurate, amorphous; methiodide, m. 251°; Bz derivative, by heating I and Bz2O 4 hrs. at 100°, m. 225°, [α]26D -3.37° (0.3075 g. in 10 cc. EtOH) (chloroaurate); Me derivative, from I and CH2N2, m. 175° (HCl salt, m. 252°; semicarbazone, decomps. 250-2°); oxime, m. 254° (decomposition); semicarbazone, decomps. 264°. Catalytic reduction of I according to Skita gives the dihydro derivative (II), m. 199°, [α]16D 170.5° (0.1756 g. in 15 cc. EtOH); semicarbazone, decomps. 207°. I.HCl and Br in AcOH give 2 Br derivs., m. 138° and 205°. ClCO2Et and KOH give the compound C25H32NO2Cl, m. 166-83° (decomposition), [α]17D -108.4° (0.2265 g. in 12 cc. CHCl3). Heating I and Bz2O 6 hrs. at 150-60° gives the compound C23H22O6, m. 206°, gives a purple-red color with concentrated H2SO4 and a red-brown color with hot NaOH. Zn distillation of I gives phenanthrene and Me3N. Reduction of I with amalgamated Zn and HCl gives desoxytetrahydrosinomeninc (III), m. 150-1°, crystallizing with 0.5 H2O, [α]21D 48.20° (0.1774 g. in 15 cc. EtOH); III salt, m. 250-1°; methiodide, m. 265°; does not react with Co reagents; III is the optical antipode of dihydrothebacodine (Speyer and Slebert, C. A. 15, 3975); a mixture of the 2, crystallized from Me2CO, is optically inactive. III.MeI and KOH, heated until a brown oil seps., gives des-N-methyldesoxytetrahydrosinomenine (IV), m. 140°, [α]21D -41.59° (0.1635 g. in 20 cc. MeOH); methiodide, hygroscopic; transformed into the chloride and heated with KOH, there results the compound V, pale yellow, m. 93°, [α]17D -181.6° (0.1564 g. in 20 cc. EtOH) and Me2N V is stable toward cold KMnO4 but on boiling a compound, m. 115°, is obtained; V is not changed by boiling with Ac2O for 15 mins. Reduction of II with Na-Hg gives the compound C18H25NO3, m. 92-105° (decomposition), [α]20D

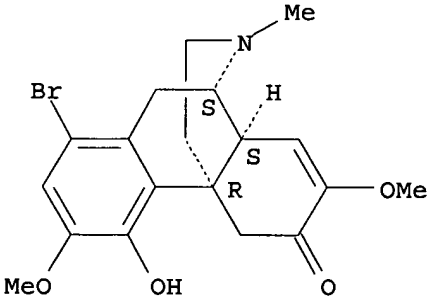
32.02 (0.1374 g. in 20 cc. EtOH); methiodide, m. 268-72°, [α]29D 23.9° (0.1548 g. in 20 cc. MeOH). This is des-methoxydihydrosinomeninol and is the optical antipode of the reduction product of dihydrothebainone (dihydrothebainol, m. 144°, [α]25D -46.2°; methiodide, m. 278° (decomposition), [α]29D -24.25°), since a mixture of the 2 is optically inactive. Reduction of I with NaHg gives the amorphous base, C14H25NO2, m. 180°, [α]27D -11.24° (0.1424 g. in 20 cc. EtOH). Heating 9 g. Na homoveratrumate and 9 g. o-nitroveratrumic aldehyde in 50 cc. Ac2O 50 hrs. at 110-20° gives α-3,4-dimethoxyphenyl-2-nitro-3',4'-dimethoxycinnamic acid, yellow, m. 191-2°; reduction with FeSO4 and NH4OH gives the 2-amino derivative, yellow, m. 146°; the diazo compound gives a mixture of 3,4,5,6-tetramethoxyphenanthrene -9-carboxylic acid (VI), m. 234°, and the 3,4,6,7-tetra-MeO derivative, m. 210°. The latter, heated with AcOH 20 hrs. at 250-60°, gives 3,4,6,7-tetramethoxyphenanthrene, m. 124-5°, identical with dimethylsinomenol (cf. Goto, J. Agr. Chemical Society Japan 2, Number 17). α-3',4'-Dimethoxy-6'-bromo-2-nitro-3,4-dimethoxycinnamic. acid, yellow, m. 216°; 2-NH2 derivative, yellow, m. 187°; 8-bromo-3,4,5,6-tetramethoxyphenanthrene -9-carboxylic acid, m. 187-8° (decomposition); reduction gives VI. Catalytic reduction of thebainone with Pd gives β-dihydrothebainone, m. 76°, [α]27D -83.94° (0.2323 g. in 20 cc. EtOH); picrate, yellow, m. 245°; semicarbazone, m. 199-201° (decomposition). Reduction of dihydrohydroxycodeinone according to Clemmensen gives dihydrohydroxythebacodine, m. 138-9°, [α]25D -58.15° (0.1135 g. in 20 cc. Me2CO). 1 (5 g.) and 6.2 g. AgNO3 in H2O give, after 36 hrs., the nitrate, decomps. above 280° of dehydrosinomenine, m. 218-20°, [α]12D 97.58° (0.1222 g. in 30 cc. MeOH). Catalytic reduction (Pd) gives isodihydrosinomenine, C19H25NO4, decomps. 271°, [α]24D 171.16° (0.1579 g. in 20 cc. EtOH); methiodide; oxime, m. 245-50° (decomposition). This compound also results by the action of AgNO3 on II; a 2nd product, insol. in Me2CO, is apparently 2C19H25NO4, m. 270°, [α]13D 113.8° (0.0914 g. in 20 cc. MeOH). Thebainone and AgNO3 give Ψ-thebainone, C19H21NO2, decomps. 227°, [α]16D -339.5° (0.1352 g. in 20 cc. Me3CO); semicarbazone, decomps. above 290°; dihydro derivative, m. 270° (decomposition), [α]26D -71.77° (0.1045 g. in 20 cc. Me2CO).

IT **847941-31-5**, Sinomenine, bromo- (isomers)

RN 847941-31-5 CAPLUS

CN Sinomenine, bromo- (3CI) (CA INDEX NAME)

Absolute stereochemistry.



L4 ANSWER 10 OF 10 CAPLUS COPYRIGHT 2006 ACS on STN

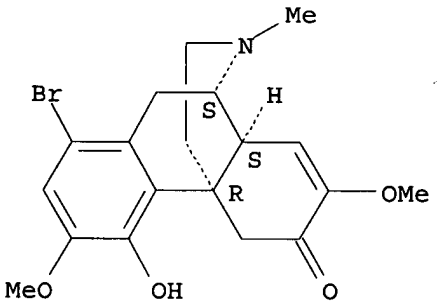
ACCESSION NUMBER: 1927:13499 CAPLUS

DOCUMENT NUMBER: 21:13499

10/536,613

ORIGINAL REFERENCE NO.: 21:1655h-i,1656a
TITLE: Sinomenine and dehydrosinomenine
AUTHOR(S): Goto, Kakuji
SOURCE: Proc. Imp. Acad. (Japan) (1926), 2, 7-9
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
AB cf. C. A. 18, 2710, J. Agr. Chemical Society Japan 1, 3, 50, 89(1925); Kondon. Ochiai and Nakajima. C. A. 18, 442. Sinomenine (I), C19H23NO4. m. 162°, [α]D20 -73.92°, contains 2 MeO groups, 1 CO2H and 1 HO; it shows the characteristic color reactions of phenols. Reduction gives hydrosinomenine, C19H25NO4, m. 201°, [α]D20 193.58°; methiodide, m. 268° (decomposition); oxime, m. 211°; semicarbazone, m. 209° I.HCl in AcOH gives 2 Br derivs., m. 153°, [α]D25 -2.62°, and m. 421°, [α]D25 14.65°; only the lower melting form gives the phenolic reactions. Dehydrosinomenine, C19H21- NO4, m. 245°, [α]D25-149.97°, occurs in nature with I but in much; smaller quantity; it is formed by oxidizing I with FeCl3, AuCl3, KMnO4, etc.; HCl salt, m. above 285°; methiodide, m. 261°; oxime, m. 265° (decomposition); semicarbazone, m. above 285°. Boiled with 66% KOH for 2 hrs., I gives MeEtNH and sinomenol, C10H14O4, m.176°; it gives 2 di-Me derivs., m. 115° and 240°, 2 di-Bz derivs., m. 206° and 260° and a di-Ac derivative, m. 149°. Distillation with Zn dust gives phenanthrene. Thus I belongs to the tetrahydroisoquinoline alkaloids of the phenanthrene group and sinomenol is a dihydroxydimethoxyphenanthrene with the HO groups in the a-positions.
IT **847941-31-5**, Sinomenine, bromo- (isomers)
RN 847941-31-5 CAPLUS
CN Sinomenine, bromo- (3CI) (CA INDEX NAME)

Absolute stereochemistry.



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L3 23 S L1 FULL

FILE 'CAPLUS' ENTERED AT 14:06:30 ON 19 APR 2006
L4 10 S L3

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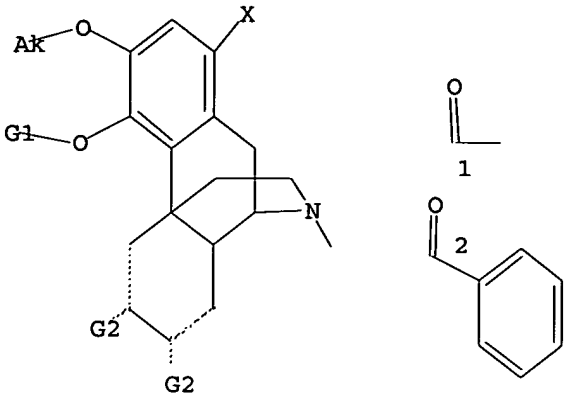
L1 STR



G1 H,[@1],[@2]

G2 O,N

Structure attributes must be viewed using STN Express query preparation.

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